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Publication date:
2010

Document Version
Publisher's PDF, also known as Version of record

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ISSN 1901-726X
DCE Technical Report No. 088

AALBORG UNIVERSITY
Department of Civil Engineering

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Geotechnical Engineering Group

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Published 2010 by
Aalborg University
Department of Civil Engineering
Sohngaardsholmsvej 57,
DK-9000 Aalborg, Denmark

Printed in Aalborg at Aalborg University

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Chloride concentration and pHs influence on the Atterberg limits of Søvind Marl

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June 9^{th} 2010

Abstract

The Atterberg limits play a great role in the assessment and classification of soils. The pore water and it components have a great influence on the behavior of the clay. When finding the Atterberg limits, de-ionised water is used to homogenize the clay. De-ionised water badly resembles the pore water in the soil. It is therefor tested how using de-ionised water and a Saline solution resembling the pore water yields different results during laboratory testing.

First the Atterberg limits are found using Saline solutions with a Chloride concentration between 0 % and 8 % and a constant pH that resembling the pH of the pore water, to determine the influence of Chloride in the water used during laboratory testing. Following the Atterberg limits are found and compared using both de-ionised water and a Saline solution with a Chloride concentration and pH resembling the pore water.

It is found that for Søvind Marl, there is a correlation between the liquid limit found and the Chloride concentration and pH of the Saline solution used in laboratory testing, differences in the liquid limit of up to 30 % is observed.

Keywords: Søvind Marl, Liquid limit, Chloride concentration, pH

1 Introduction

The behavior of clay depends greatly on the structure of the clay minerals. It is therefor important to know the composition of the clay. Thøgersen (2001) showed that Osmotic pressure had an influence on the behavior of clays when conduction Triaxial tests. The Osmotic pressure develops when there is a difference in the ion concentration of the pore water and the added. Rankka et al. (2004) showed that the salt concentration in the pore water had an influence on the behavior of quick clay in Sweden. Similar experiences have been made with quick clay in Norway.

When finding the liquid limit, w_L, and the plastic limit, w_P, of a clay, it is stated by the *Danish Standards Association* that de-ionised water is to be used. During a serie of tests, the influence of the Chloride concentration and the pH have on the Atterberg limits have been documented. This is done by comparing the Atterberg limits found when adding respectively de-ionised water and a Saline soultion with the right Chloride concentration and pH. The in-

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fluence found is the combined influence of the change in Chloride concentration and pH, and based on the laboratory test made for this paper, it is not possible to separate the influence of the change in Chloride concentration and the changed pH.

The used Saline solutions were made by adding Sodium Chloride, $NaCl$, to de-ionised water to change the Chloride concentration, and the pH was changed be adding Hydrochloric acid or Sodium hydroxide to respectively lower or raise the pH.

2 Clay Mineralogy

Mineralogy is the prime factor controlling the physical and chemical properties of a soil. Clay minerals are developed by chemical weathering of rocks. The crystal lattice is made of elementary layers. The layers can be divided into octahedral and tetrahedra layers. Clay minerals are made of combinations of these layers.

An octahedral unit consists of 6 oxygen atoms or hydroxyl groups placed octahedrally around a cation of magnesium or aluminum. Octahedral layers are made when the edge of a molecule bindes with the edge of another molecule. A tetrahedral unit consists of 4 oxygen atoms placed around a silicum, figure 1. Tetrahedrally layers are formed when three of the four oxygens are shared to form a hexagonal net. The stability of the molecule structure depends on who well the cathodic ion fits between the oxygens.

Clay minerals are divided into two groups. 1:1 groups consist of an octahedral and a tetrahedra layer, and the 2:1 groups consist of one octahedral layer and two tetrahedra layers. The group of 2:1 minerals are more heterogeneous compared to the 1:1 group, and represented by more types of minerals. Some of the most common clay minerals are Kaolinite, Illite and Smectite. [Rankka, 2004] The composition of these clay minerals can be seen in figure 2

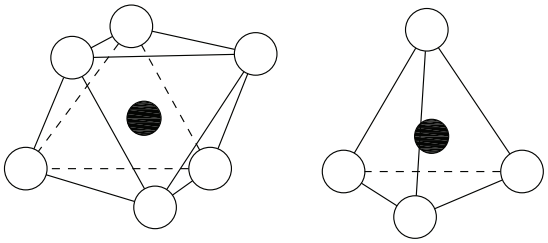

Figure 1: An octahedral unit, ○ - Hydroxyls, ● - Aluminums or magnesiums, and a tetrahedral unit, ○ - Oxygens, ● - Silicons. After: [Thøgersen, 2001, page 17–18]

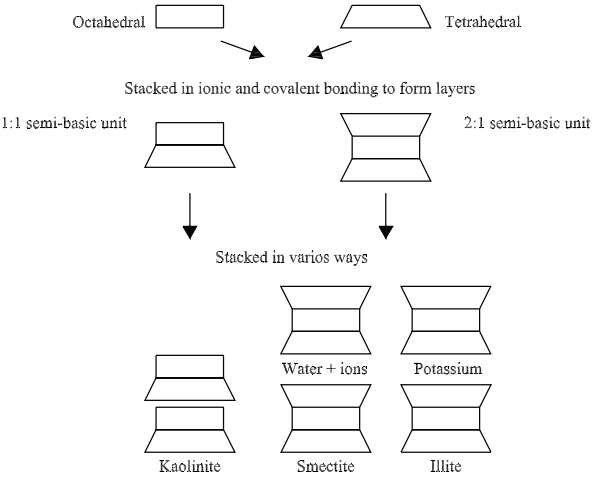

Figure 2: Composition of three of the most normal clay minerals. A simplified picturing has been used to symbolize the octahedral and tetrahedral layers. After: [Thøgersen, 2001, page 19]

2.1 Permanent Charge

The Kaolinite mineral is the most common mineral in the 1:1 group. The electrical repulsion of the Kaolinite is small. The units can therefor be held together by the Van der Waals forces, the attractive or repulsive forces

between molecules, that work between the units. Water and positively charged ions can as a result not penetrate in between the units, thereby preventing expansion of the mineral. Only a small isomorph substitution occur. The Illite minerals is a very common mineral, that belongs to the 2:1 group. Cations are held in between the units, which thereby hold the unit together. An isomorph substitution can take place in the tetrahedra layers, giving the surface a relative large charge density. Potassium ions works as compensation cation between the units, and the units will not expand. The Smectite minerals belongs to the 2:1 group. It has the oxygen atom on the outside, giving the unit a negativ charge. The Van der Waals forces is not strong enough to withstand the repulsion, making water or cations able to penetrate in between the units. This gives the Smectite minerals a tendency to swell, dependent on the water content and the ions surrounding the mineral. An extensive isomorph substitution can occur in the octahedral layer, giving the outside of the unit a small negative charge.

2.2 Variable Charge

The variable charge on a clay mineral is pH dependent. At low pH values a positive charge is developed, and at a high pH Value negative charges is developed. This effect the total charge of a unit. In environments with a decreasing pH value, the charge can change from negative, with substitution of cation capacity, to a positive charge with substitution of anion capacity.

The contribution that the pH dependent charge brings to the total charge depends on the relation between the permanent charge and the pH dependent charge. The pH dependency of Kaolinite is high, up to 50 %, whereas it is only 5 – 10 % for Smeciti. Illite has a medium dependence of the pH. This suggest that the permanent charge is the more predominant charge with Smecite then with Kaolinite.

Exchangeable cations in the clay minerals are defined as the cations that can be removed by neutral salt solutions, where as soluble salts can be removed by water. Ions of different types can replace each other, trivalent cations, like Fe^{3+} or Al^{3+}, are held more tightly than divalent cation, Mg^{2+}, which again are hold tighter then monovalent cations. The rate of displacement depende on how many different ion types there are and their size and valense. The Cation Exchange Capacity, CEC, expresses the cations capacity to exchange. The ability is dependent on the total charge of the unit, and therefor also dependent on the pH. The CEC is therefor determined at a neutral pH (7). The CEC for Smectite is large, between 80–120 $\frac{gmol(+)}{kg}$ and only 1–10 $\frac{gmol(+)}{kg}$ for Kaolinite.

2.3 Osmotic Pressure

Clay minerals most often have a natural negativ charge, and thereby try to repulse each other. Positive ions in the surrounding water is attracted to the surface of the clay minerals due to the negativ charge. The concentration of the cation increase when approaching a negative surface. This creates a diffuse double layer, where the ion concentration between the clay minerals is higher then in the surrounding water. When the clay minerals overlap, the diffuse double layer acts like a semi-permeable membran, this creates an osmotic pressure, which depends on the type of clay mineral and the ion concentration in the water surrounding the clay. [Thøgersen, 2004]

A summery of the parametres for Illite, Smectite and Kaolinite can be seen in table 1

3 Søvind Marl

An analysis of the composition of the clay minerals in the Søvind Marl from Århus harbor has been carried out by the University of Copenhagen [Balić-Žunić, 2008]. The results can be seen in table 2. The parts of the clay minerals are of the clay content, and not the total soil sample.

Table 2: The composition of the clay minerals in Søvind Marl from L*H 11.

Depth	15	30	45	60
Clay	95.6	72.8	76.4	74
Kaolinite	19	12	14	15
Illite	33	15	12	17
Smectite	44	34	42	33
Calcite	2	25	30	34
Quartz	2	1	1	1
Siderite	-	7	1	-
Rhodochrosite	-	6	-	-

A clear change in the soil composition is seen between the sample from a depth of 15 m to the sample from a depth of 30 m. The clay fraction drops from 95 % to 73 %, after which it is stable. It is seen that the primary clay mineral is Smecite, but also large amounts of Kaolinite and Illite is present in all of the samples, and in the samples from depths of 30 m or deeper Calcite is also present in a large amount.

The water content of the Søvind Marl is shown in figur 3. There is a drop in the water content from 65 % at a depth of 12 m to 35 % at 22 m, where after the water content becomes stable.

The Chloride concentration of the pore water has been measured, as described in *Manual for measurement of Chloride Concentration in pore water* [Grønbech, 2010(a)]. Figur 4 shows the Chloride concentration dependent on the depth.

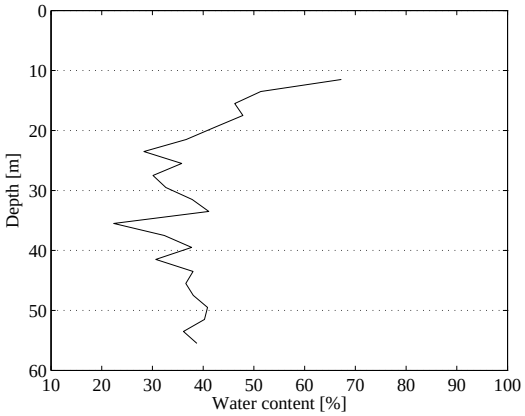

Figure 3: Water content at L*H 11.

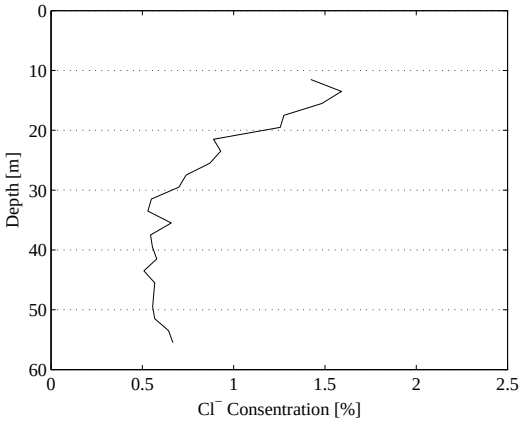

Figure 4: Chloride concentration at L*H 11.

At depths between 12 m to 27 m the Chloride concentration drops from 1.5 % to 0.5 %, where after is becomes stable.

The pH of the Søvind Marl can be seen in figure 5.

Table 1: Parametres describes along with the specifik surface of the clay minerals. After [Thøgersen, 2004, p. 30]

Characteristic	Kaolinite	Smectite	Illite
Mineral group	1:1	2:1	2:1
Permanent charge	≈ 0	0.25–0.6	0.7–1.0
CEC $[\frac{gmol(+)}{kg}]$	1–10	80–120	20–40
Specific surface $[\frac{m^2}{g}]$	18–20	600–800	70–120
Expansion	No	Yes	No
pH dependent charge	Extensive	Minimal	Medium

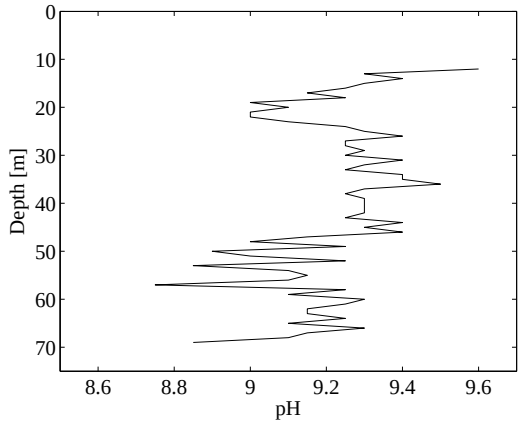

Figure 5: The pH at L*H 11.

4 Tests

Grønbech et al. (2010) showed that the liquid limit found using the Casagrande Cup and the Fall Cone is comparable. Both test procedures were used to find the liquid limit, this to see if the test methods were influenced by the difference in sample water. To obtain the desired Chloride concentration in the Saline solution Sodium Chloride, $NaCl$, was used. The sample water was prepared as described in *Manual for preparation of Saline Solution* [Grønbech, 2010(b)].

The variation of the Chloride concentration were made to see in which extend an increasing Chloride concentration had an influence on the liquid and plastic limit.

Two series of tests was made. In the first serie of tests, one sample from a depth of 23 m was divided into 8 equal samples. Each sample was added a Saline solution with Chloride concentration between 0 % to 8 %. The used Chloride concentrations and the needed amount of $NaCl$ to obtain the concentration can be seen in table 3

Table 3: Chloride concentrations used.

Cl^- [%]	$NaCl$ $[\frac{g}{liter}]$	pH
0	0	9.2
0.5	8.24	9.2
1	16.49	9.2
2	32.97	9.2
3	49.46	9.2
4	65.94	9.2
6	98.91	9.2
8	131.88	9.2

The second serie was a serie of 10 samples from different depths from L*H 9. Each sample was divided into two equal samples, where deionised water was used to homogenize one, and a Saline solution with a Chloride concentration of 0.4 % and a pH of 9.2 was used to homogenize the other.

5 Results

The results from the first serie, where a Saline solution, with a Chloride concentration varying from 0 % to 8 % and a constant pH of 9.2, was used can be seen in figure 6.

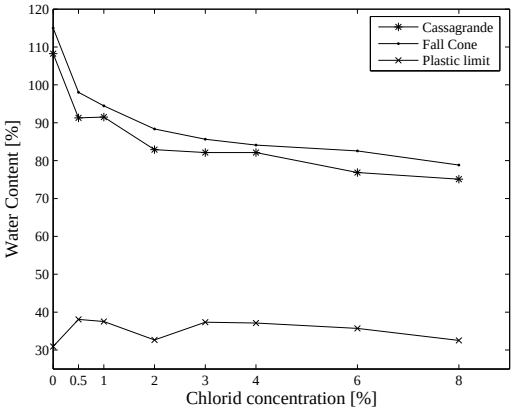

Figure 6: The variation of the liquid and plastic limit in the first serie, dependent on the Chloride concentration of the added Saline solution.

When observing the liquid limit, it is seen that a drop occurs with the presence of even a small Chloride concentration. The liquid limit decreases with an increase in the Chloride concentration of the added water to around 2–3 %, where after the liquid limit becomes more stable, but with a small tendency to fall.

The plastic limit varies around 35 %, and it shows a small tendency to decrease when the Chloride concentration of the Saline solution increases.

The difference in percentage from the liquid limit found with a Saline solution with a Chloride concentration of 0 % is listed in table 4. A difference of the liquid limit of up to more then 30 % is noticed.

The liquid and plastic limit from of the second serie of test, where a Saline solution resembling the pore water and de-ionised water were used, is illustrated in figur 7.

Table 4: The variation of the liquid limit dependent on the Chloride concentration of the Saline solution.

	Fall Cone		Casagrande	
Cl^-	w_L	Difference	w_L	Difference
[%]	[%]	[%]	[%]	[%]
0	115.0	-	108.3	-
0.5	98.0	14.8	91.3	15.7
1	94.5	17.9	91.5	15.5
2	88.4	23.2	82.9	23.4
3	85.6	25.5	82.1	24.1
4	84.1	26.9	82.1	24.1
6	82.6	28.2	76.9	29.0
8	78.8	31.5	75.1	30.6

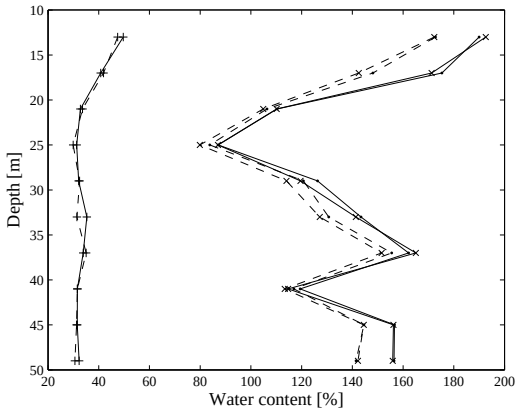

Figure 7: The liquid and plastic limit of the second serie. Legend: — : De-ionised water, - - : Saline Solution, · : Fall Cone, x : Casagrande, + : Plastic limit.

Also here is the liquid limit found using a Saline solution consistently higher then the liquid limit found using de-ionised water. The differences of the liquid limits is significant, and the difference is a high as 17 %. The differences can be seen in table 5.

Table 5: The difference in the liquid limit when homogenized with respectively de-ionised water and a Saline solution.

	Fall Cone			Casagrande		
Depth [m]	$w_{L(De-ionised)}$ [%]	$w_{L(Saline)}$ [%]	Difference [%]	$w_{L(De-ionised)}$ [%]	$w_{L(Saline)}$ [%]	Difference [%]
13	190.0	172.8	9.1	192.6	172.3	10.5
17	175.3	148.1	15.5	171.3	142.5	16.8
21	110.3	106.3	3.6	110.2	104.9	4.8
25	87.1	83.8	3.8	87.0	79.9	8.2
29	126.3	120.7	4.4	119.6	114.0	4.6
33	143.4	130.7	8.8	141.4	127.1	10.1
37	162.2	155.5	4.1	165.0	151.5	8.2
41	119.4	116.9	2.1	114.7	113.4	1.2
45	156.6	144.5	7.7	156.2	144.5	7.5
49	156.4	141.5	9.5	155.9	142.2	8.8

6 Discussion

The purpose of this paper has been to clarify the influence of the Chloride concentration of the water added when finding the Atterberg limits of Søvind Marl .

When de-ionised water is added under the homogenization of the clay for the purpose of finding the liquid limit, a dilution of the various salts in the pore water occurs. This has an effect on the behavior of the clay, and thereby the liquid limit.

A difference of the liquid limit of more then 30 % has been found during a serie of tests where the liquid limit was found under changing Chloride concentration in the water used to homogenize the Søvind Marl. A large drop occur when the Chloride concentration changes from 0 % to 2–3 %, whereafter only a small decrease in the liquid limit is noticed when the Chloride concentration increases further. The Chloride concentration was shown to have a small influence on the plastic limit, which also decreased with an increasing Chloride concentration.

A serie of tests on Søvind Marl from different depths and clay mineral composition was made with both a Saline solution resembling the pore water of the Søvind Marl and de-ionised water. It was found that the dependency of the Chloride concentration and pH depends on the clay minerals present at the clay. A difference of 17 % was found in at a depth of 17 m, where the clay concentration was high, over 95 %. At this depth the concentration of Kaolinite, Illite and Smectite was dominant, representing 96 % of the clay minerals. Using the parameters listed in table 1 to compare tabel 2 and tabel 5, it shows that the difference in the liquid limit is dependent on the clay minerals.

To obtain the behavior most resembling the clays behavior in situ, the Chloride concentration and the pH should be as close to that of the pore water as possible.

7 Literature

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